Group 8-10 complexes of pyridyl-phosphinimines and chiral bis-diiminophosphoranes.

Ramadan Altwer

University of Windsor

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Group 8 - 10 Complexes of Pyridyl-phosphinimines and Chiral Bis-Diiminophosphoranes

By

Ramadan Altwer

A Thesis
Submitted to the Faculty of Graduate Studies and Research
Through the Department of Chemistry and Biochemistry
in Partial Fulfillment of the Requirements for
the Degree of Master of Science at the
University of Windsor

Windsor, Ontario, Canada
April, 2003
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Abstract

A group of exocyclic pyridyl-phosphinimine ligands have been prepared in excellent yields by oxidizing triphenylphosphine with 2-azidomethylpyridines. These ligands reacted with group 8-10 transition metals to form various late transition metal complexes (e.g. $[\text{Ph}_3\text{P} = \text{NCH}_2(2-\text{Py})]\text{NiBr}_2$ 36) which have been characterized and evaluated for olefin polymerization activity. We found that these complexes are not active for ethylene polymerization or oligomerization. In a similar sense, nickel complexes 55 and 56 were synthesized by the reaction of nickel dihalide with a chiral bis-diiminophosphorane ligands. The corresponding ligand was prepared by deprotonation of R-2,2'-diamino-1,1'-binaphthalenetriphenyldibromide by a strong base. The complexes were seemed to be inactive for ethylene polymerization, and were therefore not tested for α-olefins polymerization.
Dedication

This work is dedicated to some important people in my life. To my mother, and my father, you have always been there for me. I greatly appreciate all that you have given me. To my wife Zeneb for helping and supporting and my sons Taha Mooneb and Alla.
Acknowledgements

I wish to acknowledge a number of people who have been important to me during the past thirty highly oppressive months of my life. I am deeply thankful to Dr. Douglas W. Stephan for his guidance, encouragement and his belief in my talent. When I first came to Windsor from Libya I was surprised by the enthusiasm that he has for chemistry, despite his extremely busy schedule.

I would like to thank those people who I have worked with: Drs. Aaron Hoskin, Chris Ong, Silke Courtenay, Jim Kickham and Liam Spencer (MSc); and those who I currently work with: Dr. Pingrong Wei, Dr. Todd Graham, Dr. Denise Walsh, and Chad Beddie (PhD), Emily Hollink (PhD), Sarah Smith (PhD), Jason Masuda (PhD), Steve Clemens (MSc), Katie Chan (MSc), Lourisa Cabrera (MSc), and Jenny McCahill (MSc). Each of you has taught me something which I will remember. Equally important, I would also like to thank all the members of the Dr Loeb group. The Department of Chemistry and Biochemistry has also been a great help in making my stay here easy and enjoyable. I would especially like to thank Mike Fuerth for all his NMR assistance, and everyone in the CCC. I would also like to thank both Dr. E. Maeva and Dr C. MacDonald for their advice.

Lastly, I am also thankful for the friendships and support from all the member of University of Windsor and I will never forget those days. I am going to tell all my families in Libya how you people are friendly and helpful and thank you all for wonderful hospitality during my stay in Canada and also for Waha Oil Company in Libya for financial support.
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Abbreviations

Å  Angstrom
Ar  aryl
atm atmosphere
BM  Bohr Magneton
Bn  benzyl (-CH$_2$(C$_6$H$_5$))
br  broad
Co. company
Cp* pentamethylcyclopentadienyl anion ($\eta^5$-C$_5$Me$_5$)
d  doublet
dd  doublet of doublets
dt  doublet of triplets
°  Degree
°C  degrees of Celsius
δ  chemical shift
DEAC diethylaluminum chloride
DME dimethoxyethane
EA  elemental analysis
eq  equivalent
ETM early transition metal
F$_c$ calculated structure factor
F$_o$ observed structure factor
g  grams
<table>
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<tr>
<th>Symbol</th>
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<tr>
<td>η</td>
<td>hapto</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>i.d.</td>
<td>internal diameter</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>iPr</td>
<td>iso-propyl ((-\text{CH(CH}_3\text{)}_2))</td>
</tr>
<tr>
<td>J</td>
<td>coupling constant</td>
</tr>
<tr>
<td>LTM</td>
<td>late transition metal</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>MAO</td>
<td>methylaluminoxane</td>
</tr>
<tr>
<td>Me</td>
<td>methyl ((-\text{CH}_3))</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>min</td>
<td>minutes</td>
</tr>
<tr>
<td>mL</td>
<td>millilitre</td>
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<tr>
<td>mm</td>
<td>millimetre</td>
</tr>
<tr>
<td>mmol</td>
<td>millimoles</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>ORTEP</td>
<td>Oak Ridge Thermal Ellipsoid Plot</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl ((-\text{C}_6\text{H}_5))</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>psi</td>
<td>pounds per square inch</td>
</tr>
<tr>
<td>py</td>
<td>pyridine</td>
</tr>
<tr>
<td>R</td>
<td>agreement factor</td>
</tr>
<tr>
<td>$R_w$</td>
<td>weighted agreement factor</td>
</tr>
<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>sept</td>
<td>septet</td>
</tr>
<tr>
<td>$^1$Bu</td>
<td>tertiary butyl (-C(CH$_3$))</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>Magnetic Susceptibility</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>alpha</td>
</tr>
<tr>
<td>$\beta$</td>
<td>beta</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>gamma</td>
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Chapter One

1.0 Introduction

The 1963 Nobel Prize in chemistry was awarded jointly to Karl Ziegler and Giulio Natta for their research on catalysts for the oligomerization and polymerization of alkenes under mild conditions. Their discoveries have grown into a multi-billion dollar industry for the production of plastics, elastomers, and inexpensive feedstock chemicals for copolymers, surfactants, and other useful additives.\(^1\) Homogeneous oligomerization and polymerization catalysts, which have long remained in the shadow of their heterogeneous counterparts, have increasingly attracted the interest of industrial and academic chemists since the late 1970’s.\(^2\) The term “homogeneous” when applied to polyalkene catalysis does not necessarily mean that catalysts, reactants and products are in a single phase. Soluble polymerization catalysts, for example, become heterogeneous if the polymer precipitates from solution. Instead, we define a “homogeneous” catalyst as one having a single type of active site, resulting in far more uniform products than are possible with classical multisite heterogeneous Ziegler-Natta catalysts.\(^3\) As economics and the demands of the marketplace require more tailored preparations of polyalkenes, researchers are recognizing the importance of turning the ‘art’ of polyalkene catalysis into a science. Understanding and controlling the active catalyst species and the processes by which alkene-based macromolecules are formed offers the opportunity for preparing products with specific properties. Soon after the discovery of alkene polymerization catalysts in
the early 1950’s was the development of cyclopentadienyl-early transition metal complexes. This was sparked by the discovery of ferrocene and led to the first homogeneous polymerization catalyst, discovered by Natta and Breslow.⁴

![Catalyst Structure](image)

**Figure 1.1:** First reported homogeneous polymerization catalyst.

Complex 1 has been used extensively for mechanistic studies on ethylene insertion,⁵ and it has been found that the tightly bound cyclopentadienyl (Cp) ligands act to encapsulate the titanium atom. Nuclear magnetic resonance (NMR) and UV (ultraviolet) spectroscopic studies of 1 suggested that the aluminum component alkylates the titanocene dichloride (Cp₂TiCl₂) and that this alkylated complex was the active agent.⁶,⁷ The presence of Ti(IV) was also deemed to be important for catalyst activity: The Ti(III) complex Cp₂Ti(μ-Cl)₂AlEt₂, was isolated by Natta and polymerizes ethylene very slowly, but it was found that after the admission of oxygen to the catalyst solution resulted in an acceleration of the polymerization rate.⁸ What is now accepted as the structure of the active site was proposed in the mid-1960’s by Shilov and Dyachkovskii.⁹ They proposed a three-coordinate [Cp₂TiR]⁺ (R=alkyl) cation as the active
catalyst. Molecular orbital calculations determined this species to be an excellent candidate for alkene insertion.\textsuperscript{10,11}

\[
\begin{align*}
\text{Ti--R} + [\text{AlCl}_4]^- \\
\end{align*}
\]

\( R=\text{alkyl} \)

2

**Figure 1.2:** Shilov and Dyachkovskii cationic complex

Eisch *et al.*\textsuperscript{12} were able to trap and isolate another Ti complex as shown in Scheme 1.1 below using a nonpolymerizable alkyne.

\[
\begin{align*}
\text{Cp}_2\text{TiCl}_2 + \text{AlMeCl}_2 & \rightarrow \text{PhC≡CSiMe}_3 \\
\text{[Cp}_2\text{TiR}]^+ + [\text{AlCl}_4]^- \\
\end{align*}
\]

**Scheme 1.1:** Isolation of $[\text{Cp}_2\text{TiR}]^+$ complex by Eisch

The cationic catalyst 2 is unsuitable for commercial applications due to its facile reduction to inactive Ti(III) species in hydrocarbon solvents during the
polymerization process. It produces polymer with an activity of 50-200 g PE / mmol cat hr-bar, which is poor compared to the conventional Ziegler-Natta catalysts system.\textsuperscript{13,14} A breakthrough in this area occurred in the mid-1970’s when it was discovered that addition of stoichiometric amounts of water to the AlMe\textsubscript{3} co-catalyst produced a new type of co-catalyst named methylalumoxane (MAO), which results in a considerable acceleration in polymerization activity of these complexes.\textsuperscript{15} More advances were made by Sinn and Kaminsky\textsuperscript{16,17} who showed that reaction of the zirconocene complexes Cp\textsubscript{2}ZrCl\textsubscript{2} and Cp\textsubscript{2}ZrMe\textsubscript{2} with methylalumoxane (MAO) in toluene gave long-lived catalysts with ethylene polymerization activities as high as 2.5 x 10\textsuperscript{7} g PE/mmol cat hr-bar.

\[ \text{Scheme 1.2: Activation of Cp}_2\text{ZrMe}_2 \text{ by excess MAO} \]

The co-catalyst (MAO) 3 also can be prepared by the partial hydrolysis of trimethylaluminum and is a mixture of polynuclear aluminum species.\textsuperscript{18}

\[ \text{Al}_2\text{Me}_6 + \text{CuSO}_4\cdot5\text{H}_2\text{O} \xrightarrow{\text{toluene}} [\text{Al(Me)O}]_n \]

\[ n=5-25 \]

\[ 3 \]

\[ \text{Scheme 1.3: Preparation of MAO.} \]
The ancillary ligands in polymerization-active metal complexes have four important roles: (1) control over the metal coordination number, (2) control over the geometry about the metal centre, (3) control over the formal oxidation state of the metal, and (4) to provide steric protection of the active site of the catalyst, which in some cases can influence the stereoselectivity.\textsuperscript{19} The modification of metallocene catalysts led to the development of new kind of non-metallocene based complexes for olefin polymerization such as constrained geometry catalyst (CGC) which was designed at Dow and Exxon and is shown in Figure 1.3 below. This catalyst and derivatives showed high ethylene polymerization activity (1500 g PE/mmol cat hr·bar), in addition, this catalyst is capable of copolymerization of ethylene with 1-hexene.\textsuperscript{20,21}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{catalyst.png}
\caption{The constrained geometry catalyst (CGC)}
\end{figure}

1.1 Late Transition Metal for Olefin Polymerization Catalysts

Most of the traditional catalysts for Ziegler-Natta polymerization such as \( \text{TiCl}_4 \) and cationic early metal-containing metallocene complexes such as \( \text{Cp}_2\text{ZrCl}_2 \) have been successfully for ethylene polymerization reactions. These
catalysts suffer from high oxophilicity which causes them to be very sensitive to moisture, necessitating the use of rigorously anaerobic conditions during the polymerization process. In addition, these catalysts are poisoned by olefins containing polar functional groups. Therefore the search for alternative complexes became a priority of some research groups. It was found that late transition metal complexes offer solutions to these problems because they are generally less oxophilic and more air stable than early transition metal complexes. In addition, they are more tolerant of functional groups. For example, ruthenium metathesis catalysts maintain high activity in the presence of wide range of functional groups, including water.\textsuperscript{22} However, compared to early metal-containing metallocene systems, these late transition metal catalysts generally exhibit reduced activities for olefin insertion and β-hydride elimination typically competes with alkyl chain growth, resulting in the formation of dimmers or oligomers. This is in fact the basis for the Shell Higher Olefin Process (SHOP) developed by Keim \textit{et al.}\textsuperscript{23} This process is based on a neutral nickel catalyst \textbf{5} containing a P-O chelate that oligomerizes ethylene to form linear C\textsubscript{4}-C\textsubscript{20} chains under high ethylene pressure and temperature or in the presence of a phosphine scavenger.\textsuperscript{24}

![Figure 1.4: SHOP catalyst.](image)
1.2 Olefin Polymerization by Late Transition Metal Complexes

The field of ethylene polymerization with late metal catalysts was revitalized when Brookhart reported a new class of olefin polymerization catalyst based on nickel complexes with α-dimiine ligands.\textsuperscript{25-28} The catalysts shown in Figure 1.5 generated high molecular weight polyethylene with high activities. The nature of the polymer produced depended highly on the specific catalyst derivative and the polymerization conditions, such as, ethylene pressure and temperature. This finding led to renewed interest in late transition metal catalysts for olefin polymerization.

![Nickel α-dimiine complex](image.png)

**Figure 1.5**: Nickel α-dimiine complex.

In 1998, Brookhart and Gibson independently developed a set of late transition metal catalysts based on the 2,6-bis(iminomethyl)pyridine (BIMP) ligand. It was found that the catalytic performance of these complexes during the polymerization process depends on the type of substituents on the imino nitrogen atoms. The Ni and Pd containing diimiine systems show mild activity compared to early transition metal metallocene species such as Cp₂TiCl₂, while the Fe-based catalysts reported by Brookhart and Gibson\textsuperscript{29-32} exhibit extraordinary
activity comparable to metallocene complexes. The Co-based analogues are less active.

![Chemical Structure](image)

\(M=\text{Fe, Co.}\)

**Figure 1.6:** 2,6-bis(iminomethyl)pyridine complexes with (BIMP) ligand.

Recently, Brookhart \(^{33,34}\) has developed another neutral Ni (II) catalyst system 8 Figure 1.7 that does not require the addition of co-catalysts. Brookhart has found that the nickel containing five membered monoanionic chelate N-O ring systems have a remarkable activity for ethylene polymerization. The key features of this ligand are a sterically hindered N-bound aryl group, and complete conjugation between the N and O atoms. This system is highly active and produces polyethylene with an activity of 8800 g PE/mmoll cat hr bar without the addition of a co-catalyst under optimized conditions. It seems that, with right choice of ligands, these late transition metal catalysts might offer an excellent and economical option to the metallocene catalytic system.
**Figure 1.7:** Nickel complex containing chelate N-O ring systems

1.3 More Developments in Late Transition Metal Catalysis

One of the latest development of the area of the late transition metal catalysis was done by Grubbs *et al.*, who was found that a N-O salicylaldiminato ligand could react to form a single-component nickel(II) catalysts which is similar to the complex Keim reported previously.

**Figure 1.8:** Ni(II) single-component catalysts
Activation of 9 with MAO produce highly linear polyethylene with 5-20 branches per 1000 carbon atoms with average $M_w > 250,000$. Also these species have a long lifetime and are capable of polymerizing ethylene with activities up to 6400 g·PE/mmol cat·hr at 250 psig of ethylene without using co-catalyst. These values are equivalent to the active $\text{C}_2\text{ZrCl}_2$ metallocene catalyst and other late transition metal catalysts such as Brookhart $\alpha$-diimine system.\textsuperscript{36}

Gibson \textit{et al.}\textsuperscript{37} reported in 2001 that the introduction of a bulky aryl group on the site adjacent to the oxygen donor group in the SHOP catalyst (compound 5 shown previously) resulted in a dramatic enhancement in activity. Activation of 10 with MAO in toluene produced 400 g PE / mmol cat hr·bar without using a phosphine scavenger.

\begin{center}
\textbf{Figure 1.9:} Gibson Ni catalyst
\end{center}

Very recently, Changato \textit{et al.}\textsuperscript{38} reported the synthesis of a series of iron and cobalt complexes bearing 2,6-bis(imino)pyridyl ligands with fluoro substituents in different positions on the imine aryl group as shown below. These complexes are analogous to iron and cobalt complexes with mono-alkyl
substituted bis-(imino) pyridyl ligands which were reported by both Brookhart and Gibson.

The iron complex oligomerized ethylene with high activity (11.1x 10^7 g/mmol. cat. hr. bar) when activated with MAO at 60°C and 10 atm of ethylene pressure. However, this activity depends on the position of fluorine atom on the aryl ring. The cobalt analogues are inactive for ethylene oligomerization.

1.4 Mechanistic Studies of Ethylene Insertion

The ethylene insertion mechanism in late transition metal catalysts has been studied by Brookhart\textsuperscript{39} (using the neutral Ni α-diimine complexes) and shows a resting state where an alkyl-ethylene species 12 is present, as shown below in Scheme 1.4. Migratory insertion results in species 13, which has a vacant coordination site that can bind another ethylene molecule. This process of coordination and insertion can continue to create a linear alkyl unit. Alternatively, 13 can β-hydride eliminate to yield the olefin hydride, species 14. The hydride complex can undergo reinsertion with the opposite regiochemistry, introducing a branched alkyl group as in 16. In a chain transfer process,
complex 15 can undergo olefin insertion and coordinated another C₂H₄ ligand to yield 18 which can initiate a new chain.

Scheme 1.4: Proposed mechanism of LTM olefin polymerization.

Brookhart found that the α-diimine complex systems are highly dependent on the steric bulk on nitrogen donor atom which has significant effect on both associative displacement and chain transfer. However, as most of the late transition metal catalysts are square planar in character, any substituents on the aryl ring lying perpendicular to the square plane suitably block the axial site close to the olefin. This allows the rate of chain propagation to be faster than the rate
of chain migration, which results in the formation of high molecular weight polymer.\textsuperscript{40}

![Diagram of ligand geometry about the Ni α-dilimine complex (R=Pr)]

**Figure 1.10:** The ligand geometry about the Ni α-dilimine complex ($R^1$Pr)

### 1.5 General Synthesis of Phosphinimine Ligands

In 1919 Staudinger discovered that P(III) compounds are readily oxidized by organic azides to form dinitrogen and iminophosphorane species.\textsuperscript{41} Iminophosphoranes are widely used in the synthesis of amides, amines, and a variety of compounds containing carbon-nitrogen double bonds. The mechanistic pathways of this reaction are based on a two-step process as shown below in Scheme 1.5 beginning with electrophilic attack on a trivalent phosphorus atom by an organic azide. An intermediate phosphazide molecule is formed, which can then eliminate dinitrogen to form a phosphinimine functional group.

\[
\begin{align*}
N_3R' + PR_3 &\rightarrow R'\overset{\text{N}}{\text{N}}\overset{\text{PR}_3}{\text{PR}_3} \\
\overset{\text{N}}{\text{N}}\overset{\text{PR}_3}{\text{PR}_3} &\rightarrow R'\overset{\text{N}}{\text{N}}\overset{\text{PR}_3}{\text{PR}_3} + \overset{\text{N}}{\text{N}}\overset{\text{N}}{\text{N}}
\end{align*}
\]

**Scheme 1.5:** Mechanism of the Staudinger reaction.
Other oxidative imination reactions of phosphorous containing compounds were published in 1965 by Kirsanov.\textsuperscript{42} This reaction includes the imination of phosphorus pentachloride and similar derivatives with compounds containing amino groups.

\[ R_3PCl_2 + NH_2R \rightarrow R_3P=NR-R' + 2HCl \]

**Scheme 1.6:** The Kirsanov reaction

1.6 Previously Reported Phosphinimine Containing Late Transition Metal Complexes

There are several examples of phosphinimine complexes showing different coordination geometries to metal centers, among of theses complexes only few have been tested for olefin polymerization. Brookhart\textsuperscript{43-47} and Gibson\textsuperscript{48} both reported the synthesis of group 8-10 metals with bis (iminophosphoranyl) pyridyl compound 19.

![Phosphinimine complex](image)

Ar = 2,6-\textsuperscript{1}Pr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}

19

Activation of 19 with MAO in toluene at 50°C at 10 bar ethylene pressure resulted in activities of 5-30 g PE/ mmol cat.hr.bar. Iron complexes with the same
ligand and polymerization conditions showed an activity of 6 g PE / mmol cat hr-bar. The polymer produced by the Fe complex had an average molecular weight of 382,000 g/mol. However, these complexes showed no polymerization activity where the ethylene pressure drops down to one atmosphere because of the insolvability of the metal complexes in the solvent used. The Pd analogues were inactive. Additionally, Stephan et al.\textsuperscript{49} have reported group 6 and 8-10 heterocyclic phosphinimine complexes shown in Figure 1.11, but these species do not polymerize ethylene upon activation with MAO.

\begin{center}
\includegraphics[width=\textwidth]{ligands.png}
\end{center}

\begin{flushleft}
R' = H, Me, SiMe\textsubscript{3}, Bn, Ph  
Ar = 2,6-Me\textsubscript{2}Ph, 2,6-Pr\textsubscript{2}Ph  
M = Ni, Fe, Pd  
X = Br, Cl
\end{flushleft}

\textbf{Figure 1.11:} Heterocyclic phosphinimine complexes.

Recently, Bochmann \textit{et al.}\textsuperscript{50,51} reported the synthesis of bi- and tri-dentate iminophosphoranes with bulky substituents on the nitrogen atoms. These ligands quickly form chelate complexes with variety of transition metals, such as Ni, Pd, Co, and Fe. The Ni bis(iminophosphoranyl)methaneide complex \textbf{22} shows sufficient charge delocalization compared to the main group compounds with
these ligands. The Co and Fe complexes 23 show a modest ethylene polymerization activity of 5 g PE/mm mol cat hr·bar at 50 °C and 10 bar ethylene pressure for the Co complex and 30 g PE / mmol cat hr·bar for Fe species under the same conditions.

Figure 1.12: Bochmann's complexes
1.7 Scope of This Work

This thesis describes the syntheses of numerous substituted pyridyl-phosphinimine and chiral 1,2-diiminophosphorane ligands, and the reactions of these ligands with some group 8-10 transition metals. This work includes the characterization of these complexes by NMR spectroscopy, elemental analyses, IR spectroscopy, magnetic susceptibility measurements, and X-ray crystallography. The polymerization activity of some metal complexes upon activation with MAO and diethylaluminum chloride (Et₂AlCl) will be discussed.
Chapter Two

Synthesis of Group 8-10 Pyridyl Phosphinimine Complexes:

2.1 Introduction

Many diimine ligands have been the target of development in late transition metal olefin polymerization. In particular, Brookhart found that α-diimine nickel catalysts present a high activity for ethylene oligomerization and polymerisation.30 The analogous phosphinimines are a readily accessible class of nitrogenous ligands, which have only recently been examined for their catalytic potential.52-56 This class of ligand can offer a steric environment similar to diimine ligands, but with apparent differences in donor strength and π-acceptor ability.

In this chapter, we investigate the syntheses of exocyclic pyridyl-phosphinimine ligands and their selected Group 8-10 metal complexes. The olefin polymerization activity of the metal complexes was determined in order to monitor the effects of changing the steric bulk on the pyridine part of the ligand.

2.2 Experimental Section

General Data. All preparations were performed under an atmosphere of dry, anaerobic nitrogen employing Schlenk line techniques, an MBraun inert atmosphere glovebox, or a Vacuum Atmospheres Co. glovebox. Unless otherwise mentioned, all organic chemicals were reagent grade and were used as received from Aldrich Chemical Co. All phosphines and metal compounds were used as received from Strem Chemical Co. Diethyl ether, ethanol, hexane, methylene chloride, and toluene were either dried according to literature
techniques\textsuperscript{57} or were obtained directly from an Innovative Technologies solvent purification system. 6-methyl 2-chloromethyl pyridine hydrochloride 29 and 6-phenyl-2-chloromethyl pyridine hydrochloride 34 were prepared according to literature techniques.\textsuperscript{58-59} \textsuperscript{1}H, \textsuperscript{13}C\textsuperscript{1}H\}, and \textsuperscript{31}P\textsuperscript{1}H\} NMR spectra were recorded on a Bruker Avance 300 MHz NMR spectrometer operating at 300, 75, and 121 MHz, respectively. Several \textsuperscript{1}H, \textsuperscript{13}C\textsuperscript{1}H\}, and \textsuperscript{31}P\textsuperscript{1}H\} NMR spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer operating at 500, 121, and 202 MHz, respectively. Trace amounts of protonated solvents were used as references for \textsuperscript{1}H and chemical shifts reported relative to tetramethylsilane (SiMe\textsubscript{4}). \textsuperscript{31}P\textsuperscript{1}H\} spectra were externally referenced to 85\% H\textsubscript{3}PO\textsubscript{4}. The \textsuperscript{13}C\textsuperscript{1}H\} resonances reported are all singlet unless otherwise stated. Elemental analyses were carried out by the Centre for Catalysis and Materials Research (CCMR), Windsor, Ontario, Canada. IR spectroscopy was performed on a Bruker Infrared Fourier Transform Spectrometer VECTOR 22. Unpaired electron measurements were made with a Johnson Matthey magnetic susceptibility balance (Evans design).
Synthesis of 2-azidomethyl-pyridine 2-(N3CH2) (C6H4N) (25)

To a stirred solution of 2-picolyl chloride hydrochloride (2-chloromethyl pyridine hydrochloride) (18.28 mmol, 3.00 g) in 100 ml of water was added NaN3 (21.93 mmol, 1.426 g) and the mixture was refluxed for two days. The solution was allowed to cool, and was neutralized by the addition of a solution of 2M NaHCO3, and the product was then extracted with CH2Cl2. The organic phase was dried over anhydrous MgSO4, and the solvent was removed to give brown oil 3.1 g (70%). The oil was not purified due to the risk of explosion.

1H NMR (C6D6): δ 8.45 (d, 1H, JHH = 3Hz, 1H, -py H), 7.25 (d, JHH = 1Hz, 1H, -py H), 7.09-7.06 (m, 1H, -py H), 6.98 (t, JHH = 3Hz, 1H, -py H), 4.08 (s, 2H, -CH2).

13C{H}NMR (CD2Cl2): δ 156.8, 150.2, 136.6, 122.9, 122.0, 55.

Synthesis of 2-azidomethyl-pyridine phosphinimine 2-(Ph3PNCH2)(C6H4N) (26):

To a stirred solution of compound 25 (7.40 mmol, 1.00g) in toluene (50 ml) under N2 was added PPh3 (3.70 mmol, 0.97 g). The mixture was heated to 60 °C for 6 hours and then was cooled to room temperature and the solvent was then removed under reduced pressure to give a yellow powder 0.6 g (60%).

νP=N (1360 cm⁻¹). 31P {H} NMR (C6D6): δ 7.8 (s). 1H NMR (C6D6): δ 8.48 (d, JHH = 9Hz, 1H, -py), 7.86-7.80 (m, 11H, -ArH), 7.78 (d, JHH = 6Hz, 4H, -ArH), 7.25 (d, JHH = 1Hz, 1H, -py H), 7.16 (t, JHH = 3Hz, 1H, -py H), 7.14-7.01 (m, 1H, -py H), 5.09 (s, 2H, -CH2).
Synthesis of 6-methyl-2-hydroxymethylpyridine 2-(CH$_2$O)-6-Me(C$_6$H$_3$N) (27)

Compound 27 was prepared according to a literature method$^{58}$, however, NMR data was not reported for this species. $^1$H NMR (CDCl$_3$): $\delta$ 7.56 (t, J$_{H-H}$ = 3Hz 1H, -py), 7.10 (m, 2 H, -py), 4.20 (s, 2H, -CH$_2$), 2.54 (s, 3H, -CH$_3$).

Synthesis of 6-methyl-2-chloromethyl pyridine hydrochloride (6-CH$_3$(2-py)CH$_2$HCl) (28):

Compound 28 was prepared according to a literature method$^{59}$ however, NMR data was not reported. $^1$H NMR (CDCl$_3$): $\delta$ 8.25 (d, J$_{H-H}$ = 1Hz, 1H, -py H), 7.86 (d, J$_{H-H}$ = 2Hz, 1H, -py H), 7.36 (m, 1H, -py H), 5.3 (s, 2H, -CH$_2$), 2.56 (s, 3H, -CH$_3$).

Synthesis of 6,2-azido dimethyl pyridine (6-CH$_3$CH$_2$N$_3$(2-Py))(29):

To a stirred solution of 6-Me(2-py)CH$_2$HCl, (5.58 mmol, 1.00g), in 100 ml of water was added (0.44 g 6.80 mmol) of NaN$_3$ and the stirred mixture was refluxed for 48 hours. The mixture was cooled to room temperature and then was neutralized by the addition of (1.40 g 16.66 mmol) of NaHCO$_3$, and the product was then extracted into CH$_2$Cl$_2$. The resulting solution was dried over anhydrous MgSO$_4$ and the solvent was removed under reduced pressure, yielding 0.60 g (60%) of the product as brown oil. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 7.68 (d, J$_{H-H}$ = 12Hz, 1H, -py H), 7.13 (t, J$_{H-H}$ = 3Hz, 1H, -py H), 7.09 (d, J$_{H-H}$ = 3Hz, 1H, -py H), 4.43 (s, 2H, -CH$_2$), 2.55 (s, 3H, -CH$_3$). $^{13}$C {H} NMR (CD$_2$Cl$_2$): $\delta$ 158.2, 149.2, 136.1, 122.9, 122.0, 56, 21.2.
Synthesis of 6, 2-azido dimethyl pyridine phosphinimine (2-\{(Ph3PNCH2)-6-Me(C6H5N)\}) (30):

To a stirred solution of compound 29 (3.38 mmol, 0.50 g) in toluene (50 ml) under N2 was added PPh3 (1.68 mmol, 0.44 g). The mixture heated at 60 °C for 6 hours. It was allowed to cool, and then the solvent was removed under pressure. The yellow oil was washed with hexane several times giving the product in 0.62 g 60% yield, νP=N 1358 cm⁻¹. 31P{H} NMR: (C6D6): δ 7.8 (s). 1H NMR (C6D6): δ 8.66 (d, 2H, -Ar H), 8.54 (d, JH,H = 42Hz, 2H, -Ar H), 7.85 (m, 11H, -Ar H), 7.48 (d, JH,H = 18Hz , 1H, -py H ), 7.25 (m, 1H, -py H), 7.08 (t, JH,H = 6Hz, 1H, -py H), 5.10 (s, 2H, -CH2), 2.54 (s, 3H, -CH3).

Synthesis of 6-phenyl pyridine carboxaldehyde (6-Ph(2-py)CH2O) (31):

Compound 31 was prepared according to a literature method60 however, NMR data was not reported. 1H NMR (CDCl3): δ 10.1 (s, H, -aldhy.), 8.2 (d, JH,H = 6Hz, 3H, -Ar H), 8.0 (d, JH,H = 9Hz, 2H, -Ar H), 7.5 (m, H, -py H), 7.08 (t, JH,H = 3Hz, 1H, -py H), 6.87 (d, 1H, -Py H).

Synthesis of 6-phenyl-2-hydroxymethyl pyridine (6-Ph (2-py) COH) (32):

To a solution of 31 (5.45 mmol, 1.00 g) in ethanol (100 ml) at 0 °C was added (0.21 g 5.6 mmol) of NaBH4. The solution was stirred for 1 hour, after which 100 ml of water was added. The solution was neutralized by the addition of 1.0 M aqueous HCl, and the product was extracted into Et2O. The solution was dried over anhydrous MgSO4 and the solvent was removed under reduced pressure, yielding the product as a yellow oil 0.85 g (85%). 1H NMR (CDCl3): δ 8.03 (d, JH-
\( H = 3Hz, 3H, -Ar H), 7.54 (m, 2H, -Ar H), 7.31-7.11 (m, 1H, -py H), 7.08 (t, 1H, -py H), 6.87 (d, 1H, -py H) 4.82 (s, H, -OH).

**Synthesis of 6-phenyl-2-picoylchloride (6-Ph (2-py) CH\_2Cl\_2HCl) (33):**

Compound 33 was prepared according to a literature method\(^69\) however, NMR data was not reported. \(^1\)H NMR (CDCl\(_3\)): \( \delta \) 8.03 (d, \( J_{H-H} = 3Hz, 3H, -Ar H), 7.54 (m, 2H, -Ar H), 7.31 (m, 1H, -py H), 7.08 (t, \( J_{H-H} = 6Hz, 1H, -py H), 6.87 (d, \( J_{H-H} = 3 Hz, 1H, -py H), 5.57 (s, 2H, -CH\_2).\)

**Synthesis of 6-phenyl-2- azido methyl pyridine (6-Ph (2-py) CH\_2N\_3) (34):**

To a stirred solution of 6-Ph(2-py)CH\(_2\)HCl 33 (1.78 mmol, 0.43 g), in 100 ml of water was added (0.14 g 2.5 mmol) of NaN\(_3\) and then the stirred mixture was refluxed for 48 hours. The solution was then allowed to cool and was neutralized by the addition of (1.5 g 17.5 mmol) of NaHCO\(_3\). The product was extracted into CH\(_2\)Cl\(_2\), and the solution was then dried over MgSO\(_4\). The solvent was removed under reduced pressure, yielding 0.26 g (60%) of the product as a light brown oil. \(^1\)H NMR (CDCl\(_3\)): \( \delta \) 8.03 (d, \( J_{H-H} = 3Hz, 3H, -Ar H), 7.54-7.37 (m, 2H, -Ar H), 7.31 (m, 1H, -py H), 7.09 (t, \( J_{H-H} = 6Hz, 1H, -py H), 6.87 (d, \( J_{H-H} = 1Hz, 1H, -py H), 4.52 (s, 2H, -CH\_2).\)
Synthesis of 6-phenyl-2-azido methyl pyridine phosphinimine (2-Ph₃PNCH₂)-6-Ph(C₆H₃N)) (35):

To a stirred solution of 6-Ph(2-py)CH₂N₃ 34 (2.18 mmol, 0.50 g) in 30 ml of dry toluene was added (0.15 g 0.75 mmol) of PPh₃ and the mixture was refluxed for 6 hours. It was then allowed to cool and the solvent was removed under reduced pressure, yielding a yellow solid 0.25 g (55%). \( \nu_{\text{P-N}} \) 1355 cm\(^{-1}\). \(^{31}\text{P}\) \{\( \text{H} \}\) NMR (C₆D₆): \( \delta \) 7.9(s). \(^{1}\text{H}\) NMR (C₆D₆): \( \delta \) 7.76 (m, 11H, -Ph), 7.55 (t, \( J_{\text{H-H}} = 3\text{Hz}, 4\text{H}, -\text{Ph} \)), 7.99 (d, \( J_{\text{H-H}} = 1\text{Hz} , 2\text{H}, -\text{Ar} \)), 7.35 (d, \( J_{\text{H-H}} = 2\text{Hz}, 2\text{H}, -\text{Ar} \)), 7.28 (s, 1H, -Ar), 7.38 (s, 1H, -py), 7.46 (d, \( J_{\text{H-H}} = 1\text{Hz}, 1\text{H}, -\text{py} \)), 7.44 (d, \( J_{\text{H-H}} = 1\text{Hz} ,1\text{H}, -\text{py} \)), 5.34 (s,2H, CH₂).
Figure 2.1: list of compounds
Synthesis of [Ph₃P=NCH₂(2-py)]NiBr₂ 36, [6-CH₃Ph₃P=NCH₂(2-py)]NiBr₂ 40, [6-PhPh₃P=NCH₂(2-py)]NiBr₂ 44

Compounds 36, 40 and 44 were prepared by similar methods, thus only one representative procedure is described. To (0.400 g 1.91 mmol) of NiBr₂(DME) adduct and (0.50 g 1.41, 1.35 and 1.30 mmol) of 27, 31 and 35 was added 10 ml THF. The purple suspension was stirred overnight, and the mixture was filtered to give a purple powder. **36**: Yield (55%), νᵢₚ-N 1280 cm⁻¹, μₑffective = 2.35. ³¹P {H} NMR (CD₂Cl₂): δ 41.3 (s). ¹H NMR (CD₂Cl₂): δ 8.45 (d, J₆₋₇ = 3 Hz, 1H, -py H), 7.25 (d, J₆₋₇ = 1 Hz, 1H, -py H), 7.09 (m, 1H, -py H), 6.98 (t, 1H, -py H), 4.08 (s, 2H, -CH₂). Anal. Calcd for C₂₄H₂₂N₂PNiBr₂: C; 50.13, H; 3.40, N: 4.77. Found: C; 51.00, H; 3.98, N; 5.13

**40**: Yield 60%, purple powder, νᵢₚ-N 1278 cm⁻¹. μₑffective = 2.98. ³¹P {H} NMR (CD₂Cl₂): δ 40.1 (s). ¹H NMR (CD₂Cl₂): δ 8.66 (d, J₆₋₇ = 1 Hz, 2H, -Ar H), 8.54 (d, J₆₋₇ = 24 Hz, 2H, -Ar H), 7.85 (m, 11H, -Ar H), 7.50 (d, J₆₋₇ = 2 Hz, 1H, -py H), 7.25 (m, 1H, -py H), 7.09 (t, J₆₋₇ = 6 Hz, 1H, -py H), 5.10 (s, 2H, -CH₂), 2.54 (s, 3H, -CH₃). Anal. Calcd for C₂₅H₂₃N₂PNiBr₂: C; 49.92; H; 3.82, N: 4.66. Found: C; 50.10, H; 4.12, N; 5.11

**44**: Yield 70%, purple powder, νᵢₚ-N 1270 cm⁻¹. μₑffective = 3.02. ³¹P {H} NMR (C₆D₆): δ 40.34 (s). ¹H NMR (C₆D₆): δ 7.76 (m, 11H, -Ph) 7.55 (t, J₆₋₇ = 3 Hz, 4H, -Ph), 7.99 (d, J₆₋₇ = 1 Hz, 2H, -Ar), 7.35 (d, J₆₋₇ = 2 Hz, 2H, -Ar), 7.28 (s, 1H, -Ar), 7.38 (s, 1H, -py), 7.46 (d, J₆₋₇ = 1 Hz, 1H, -py), 7.44 (d, J₆₋₇ = 4 Hz, 1H, -py), 5.34 (s, 2H, CH₂). Anal. Calcd. for C₃₀H₂₅N₂PNiBr₂ C; 54.34, H; 3.77, N; 4.22. Found C; 54.99, H; 4.17, N; 5.01.
Synthesis of [Ph₃P=NCH₂(2-py)]FeCl₂ 37, [6-CH₃Ph₃P=NCH₂(2-py)]FeCl₂ 41:

Compounds 37 and 41 were prepared by similar methods, thus only one representative procedure is described. To (0.200 g 1.57 mmol) of FeCl₂ adduct and (0.500 g 1.41 and 1.3 mmol) of 27 and 31 was added 10 ml of THF. The green suspension was stirred overnight and the mixture was filtered to give green powder 37: Yield = 60%. νₚ=ν 1231 cm⁻¹. μₑff = 4.98. ³¹P {H} NMR (br). Anal. Calcd. for C₂₄H₂₂N₂PFeCl₂ : C; 55.88, H; 4.24, N; 5.66. Found. C; 56.64, H; 4.50, N, 6.00.

41: Yield=65%, green powder, νₚ=ν 1225 cm⁻¹. μₑff = 5.11. ³¹P {H} NMR (br). Anal. Calcd. for C₂₅H₂₂N₂PFeCl₂ : C; 56.49, H; 4.47, N; 6.62. Found C; 56.61, H; 5.11, N; 6.70.

Synthesis of [Ph₃P=NCH₂(2-py)]CoCl₂ 38, [6-CH₃Ph₃P=NCH₂(2-py)]CoCl₂ 42:

Compounds 38 and 42 were prepared by similar methods, thus only one representative procedure is described. To (0.200 g 1.53 mmol) of CoCl₂ adduct and (0.500 g 1.41, 1.35 mmol) of 27 and 31 was added 10 ml of THF. The blue suspension was stirred overnight, and the mixture was filtered to give a blue powder.

38: Yield=70%, blue powder, νₚ=ν 1260 cm⁻¹. μₑff = 4.08. ³¹P {H} NMR (br). Anal. Calcd. for C₂₄H₂₂N₂PCoCl₂ : C; 57.85, H; 4.21, N; 5.62. Found C; 58.01, H; 4.24, N; 5.70.
Yield = 75%, blue powder, ν<sub>p=ν</sub> 1252 cm<sup>-1</sup>. μ<sub>eff</sub> = 5.23. <sup>31</sup>P {H} NMR (br). Anal. Calcd. for C<sub>25</sub>H<sub>22</sub>N<sub>2</sub>PCoCl<sub>2</sub> : C; 58.39, H; 4.71, N; 5.71 Found C; 58.61, H; 4.83, N; 6.19

**Synthesis of [Ph<sub>3</sub>P=NHCH<sub>2</sub>(2-py)]PdCl<sub>2</sub> 39, [6-CH<sub>3</sub>Ph<sub>3</sub>P=NHCH<sub>2</sub>(2-py)]PdCl<sub>2</sub> 43:**

Compounds 39 and 43 were prepared by similar methods, thus only one representative procedure is described. To (0.310 g 0.81 mmol) of PdCl<sub>2</sub>(PhCN)<sub>2</sub> adduct and (0.55 g 1.45, 1.48 mmol) of 27 and 31 was added 10 ml of toluene. The yellow suspension was stirred overnight, and the mixture was filtered to give yellow powder.

39: Yield = 80%, yellow powder, ν<sub>p=ν</sub> 1286 cm<sup>-1</sup>. <sup>31</sup>P {H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 36.5 (s). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.45 (d, J<sub>H-H</sub> = 3 Hz, 1H, -py H), 7.25 (d, J<sub>H-H</sub> = 1 Hz, 1H, -py H), 7.09 (m, 1H, -py H), 6.98 (t, J<sub>H-H</sub> = 3 Hz, 1H, -py H), 4.08 (s, 2H, -CH<sub>2</sub>). Anal. Calcd. for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>PdCl<sub>2</sub> : C; 52.80, H; 3.85, N; 5.13. Found. C; 53.02, H; 4.04, N; 5.42

43: Yield = 78%, yellow powder, ν<sub>p=ν</sub> 1279 cm<sup>-1</sup>. <sup>31</sup>P {H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 36.99 (s). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.66 (d, J<sub>H-H</sub> = 3 Hz, 2H,-Ar H), 8.64 (d, J<sub>H-H</sub> = 45 Hz, 2H, -Ar H), 7.85 (m, 11H, -Ar H), 7.50 (d , J<sub>H-H</sub> = 2 Hz, 1H, -py H) 7.26 (m, 1H, -py H), 7.09 (t, J<sub>H-H</sub> = 6 Hz, 1H, -py H), 5.10 (s, 2H, -CH<sub>2</sub>), 2.54 (s, 3H, -CH<sub>3</sub>). Anal. Calcd. for C<sub>25</sub>H<sub>22</sub>N<sub>2</sub>PdCl<sub>2</sub> : C; 58.39, H; 4.71, N; 5.71. Found. C; 58.61, H; 4.83, N; 6.19
Figure 2.2: Synthesis of transition metal complexes with ligands 26, 30.
**Figure 2.3:** Synthesis of Ni metal complex with ligand 35.

**Procedure for ethylene polymerization**

A 500 mL Parr stainless steel autoclave equipped with mechanical stirring and pressure gauge was heated (~110°C) under vacuum for >2 hours. The temperature of the autoclave was regulated by a thermal jacket. The autoclave was cooled to the desired temperature and 500 equivalents of MAO dissolved in toluene were added under N₂. The solution was stirred for an additional hour, and a toluene suspension of the catalyst was added. The vessel was then quickly pressurized with 300 psi of ethylene, and stirred for 30 minutes. The polymerization was stopped by venting the volatiles at room temperature, followed by quenching of the reaction solution with acidified MeOH. The resulting solution was filtered. The organic layer was separated, dried with anhydrous Na₂SO₄, filtered and the solvent removed to give traces of a sticky, gummy polymer. The trace amounts of polymer were redissolved in hexane, filtered again to remove any residual catalyst, and the solvent removed.
General Information on X-Ray Data Collection and Reduction

All X-ray data collection, data reduction, structure solution and refinement obtained in this thesis were performed by using the same method; thus only one general description is given. X-ray quality crystals were manipulated and mounted in either 0.5 mm or 0.7 mm capillaries in a glove box, thus maintaining a dry, \( \text{O}_2 \)-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART system CCD diffractometer employing graphite-monochromated Mo K\( \alpha \)-radiation (\( \lambda = 0.71073 \) Å). A hemisphere of data with 30-second exposure times was collected. Data were further processed using the SHELX crystallographic software. An empirical absorption correction was applied to the data using SADABS. The reflections with \( F_0^2 > 3\sigma F_0^2 \) were used in the refinements.

General Information of Structure Solution and Refinement

Non-hydrogen atomic scattering factors were taken from literature tabulations. Atomic positions were determined either by SHELXTL-93 direct methods or a Patterson routine with successive difference Fourier map calculations refinements were carried out by full-matrix least-squares techniques on \( F \) or \( F^2 \) minimizing the function \( \omega \left( |F_o| - |F_c| \right)^2 \) where the weight \( \omega \) is defined as \( 4F_0^2/2\sigma(F_0^2) \) and \( F_0 \) and \( F_c \) are the observed and calculated structure factor amplitudes, respectively. In the final cycles of refinements, all non-hydrogen atoms were assigned anisotropic temperature factors. Hydrogen atom positions were calculated to ride on the carbon atoms to which they were bound assuming
a C-H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 110% of the temperature factors of the carbon atoms to which they were bound. All hydrogen atom contributions were calculated but not refined. After the final cycles of refinement no chemically significant residual electron density was observed.

**X-ray Structure Determination of 36, 40, 42 and 44**

Data were collected at room temperature. No crystal decay was observed for any of the compounds. ORTEP drawings of 36, 40, 42 and 44 are shown in Figures 2.5, 2.6, 2.7 and 2.8 respectively, with 30% thermal ellipsoids. Selected bond distances and angles are listed in the caption for Figures 2.5, 2.6, 2.7 and 2.8 respectively. Other structural parameters are given in Tables 2.1 and 2.2.
### Table 2.1: Crystallographic Parameters for 36 and 40

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<td>γ(deg)</td>
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<td>Monoclinic</td>
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<td>P2$_1$/c</td>
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$^a$All data collected at 20$^\circ$C with Mo Kα radiation (λ = 0.71073 Å), $R = \sum|F_o| - |F_c|/|F_o|$, $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^2]]^{0.5}$
### Table 2.2: Crystallographic Parameters for 42 and 44

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<td>Goodness of Fit</td>
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\(^a\)All data collected at 20\(^\circ\)C with Mo K\(\alpha\) radiation (\(\lambda = 0.71073\) Å), \(R = \Sigma |F_o| - |F_c|/\Sigma |F_o|\), \(R_w = [\Sigma (\omega(F_0^2 - F_c^2)^2)/\Sigma \omega F_0^2]]^{0.5}\).
2.3 Result and Discussion

A series of 2-azidomethyl pyridines (25, 29 and 34) were prepared in reasonable yields by the reaction of the substituted pyridinium chloride precursors with NaN₃ in H₂O, as is shown below in Scheme 2.1.

Scheme 2.1: Synthesis of 2-azidomethylpyridines.

Pyridine-phosphinimine ligands (26, 30 and 35) have been successfully synthesized in reasonable yields by oxidizing PPh₃ with 2-azidomethyl pyridines in hot toluene as shown in Scheme 2.2. The ³¹P (H) spectra of all these ligands, show chemical shift resonance at 7.8 ppm, which indicates the formation of an N=P bond as we expected. The ¹H NMR spectra of compounds 26, 30, and 35 show the expected resonances, indicating the presence of a proton, a methyl or a phenyl group in the six position of the pyridine ring. The IR spectra of these ligands show a strong band between 1360-1355 cm⁻¹ consistent with the presence of a P=N bond.⁶¹

Scheme 2.2: Synthesis of substituted pyridyl-phosphinimine ligands.
The phosphinimine ligands were reacted with selected first and second row Group 8-10 metal halides in appropriate solvents to give ether paramagnetic or diamagnetic complexes. Complexes of the type PdCl$_2$(L) (39, 43) (L=26, 30) (L)NiBr$_2$ 36, 40, 44 (L=26, 30, 35), FeCl$_2$(L) 37, 41 (L=26, 30), CoCl$_2$(L) 38, 42 (L=26, 30) were prepared as shown below in Scheme 2.3 and characterized spectroscopically. The $^1$H NMR spectra data showed minor differences between the free ligands and transition metal complexes. The $^{31}$P{$^1$H} NMR spectra showed large chemical shift changes with resonances appearing at 41.3 ppm for the Ni complexes, and 36.9 ppm for Pd complexes, while the Fe and Co complexes showed broad spectra due to their paramagnetic nature.

\[
\begin{align*}
\text{R=H(26), Me(30), Ph(35)}
\end{align*}
\]

Scheme 2.3: Synthesis of substituted pyridyl-phosphinimine complexes
Figure 2.4: ORTEP drawing of 36, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Ni(1)-N(1) 1.980(4) Å, Ni(1)-N(2) 1.986(4) Å, Ni(1)-Br(2) 2.3610(2) Å, Ni(1)-Br(1) 2.3829(1) Å, P(1)-N(1) 1.607(4) Å, P(1)-C(13) 1.799(5) Å, P(1)-C(19) 1.800(5) Å, P(1)-C(7) 1.819(5) Å, N(1)-C(1) 1.475(5) Å, N(2)-C(2) 1.338(6) Å, N(2)-C(6) 1.355(6) Å, N(1)-Ni(1)-N(2) 83.69(2)°, N(1)-Ni(1)-Br(2) 118.99(11)°, N(2)-Ni(1)-Br(2) 108.59(12)°, N(1)-Ni(1)-Br(1) 125.12(1)°, N(2)-Ni(1)-Br(1) 102.95(1)°, Br(2)-Ni(1)-Br(1) 110.22(4)°.
Figure 2.5: ORTEP drawing of 40, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Ni(1)-N(1) 1.982(3)Å, Ni(1)-N(2) 2.008(3) Å, Ni(1)-Br(1) 2.3824(1) Å, Ni(1)-Br(2) 2.3874(1) Å, P(1)-N(1) 1.609(3) Å, P(1)-C(14) 1.799(4) Å, P(1)-C(8) 1.808(4) Å, P(1)-C(20) 1.816(4) Å, N(1)-C(7) 1.463(4) Å, N(2)-C5 1.343(4) Å, N(2)-C(1) 1.372(4) Å, N(1)-Ni(1)-N(2) 84.13(11)°, N(1)-Ni(1)-Br(1) 113.73(9)°, N(2)-Ni(1)-Br(1) 111.91(9)°, N(1)-Ni(1)-Br(2) 115.89(9)°, N(2)-Ni(1)-Br(2) 104.98(9)°, Br(1)-Ni(1)-Br(2) 119.82(3)°.
Figure 2.6: ORTEP drawing of 42, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Co(1)-N(1) 1.989(2) Å, Co(1)-N(2) 2.052(2) Å, Co(1)-Cl(2) 2.2330(1) Å, Co(1)-Cl(1) 2.2662(1) Å, N(1)-C(7) 1.475(3) Å, N(1)-P(1) 1.600(2) Å, N(2)-C(5) 1.347(3) Å, N(2)-C(1) 1.353(3) Å, P(1)-C(20) 1.799(3) Å, P(1)-C(8) 1.799(3) Å, P(1)-C(14) 1.806(3) Å, N(1)-Co(1)-N(2) 83.79°, N(1)-Co(1)-Cl(2) 113.18(7)°, N(2)-Co(1)-Cl(2) 116.969(8)°, N(1)-Co(1)-Cl(1) 120.52(7)°, N(2)-Co(1)-Cl(1) 103.54(8)°, Cl(2)-Co(1)-Cl(1) 114.66(4)°, C(7)-N(1)-P(1) 117.16(2)°, C(7)-N(1)-Co(1) 112.68(2)°, P(1)-N(1)-Co(1) 128.83(1)°, C(5)-N(2)-C(1) 118.90(2)°.
Figure 2.7: ORTEP drawing of 44, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Ni(1)-N(2) 2.014(1) Å, Ni(1)-N(1) 2.032(2) Å, Ni(1)-Br(1) 2.363(2) Å, Ni(1)-Br(2) 2.417(2) Å, P(1)-N(1) 1.569(1) Å, P(1)-C(13) 1.771(2Å), P(1)-C(19) 1.790(1) Å, P(1)-C(25) 1.817(1) Å, N(1)-C(1) 1.479(2) Å, N(2)-C(2) 1.331(2) Å, N(2)-C(6) 1.369(2) Å. N(2)-Ni(1)-N(1) 85.2(5)°, N(2)-Ni(1)-Br(1) 106.4(3)°, N(1)-Ni(1)-Br(1) 113.0(3)°, N(2)-Ni(1)-Br(2) 107.4(3)°, N(1)-Ni(1)-Br(2) 102.0(3)°, Br(1)-Ni(1)-Br(2) 132.62(1)°.
The formation of pyridyl phosphinimine complexes 36, 40, and 44 were verified by a single crystal diffraction studies. As we expected, the geometry about the metal center atom of these complexes are pseudo-tetrahedral with two halides and a bidentate pyridyl-phosphinimine ligand completing the coordinating sphere. The P-N bond lengths in 36, 40, and 44 ranged from 1.569(10) Å to 1.609(5) Å which indicate the presence of double bond and also agrees with the average P-N bond lengths which were reported by Stephan et al 49 for similar compounds (1.586(2) Å, and 1.615(11) Å. For the Ni complexes 36, the Ni-Br distances are similar 40 and 44, all ranging from 2.360(2) Å to 2.417(2) Å.

In contrast to the endocyclic P-ligand complexes which were reported by L. Spencer 57, these exocyclic pyridyl phosphinimine species exhibit Ni-N_py and Ni-N_phos bond lengths that are very similar to each other (36: 1.976(5) Å, 1.977(4) Å, 40: 1.983(3) Å, 2.008(3) Å, 44: 2.008(10) Å, 2.007(10) Å.

The cobalt pyridyl phosphinimine complex 42 was characterized and the geometry of this species is similar to the Ni complex 40, with average Co-Cl distances of 2.2545(13) Å and Co-N_py and Co-N_phos distances of 1.989(2) Å and 2.053(2) Å, respectively. These structural data reveal that both electronic and steric changes to the geometry of these ligands with exocyclic phosphine fragments appear to reduce steric congestion at the metal center allowing strong interactions with donor atoms. In the case of 44 in particular, we note that the angle between the planes of the pyridine ring and the phenyl substituent is 45.3°. This substituent, together with the exocyclic phosphine group, appears to create
a “protective pocket” for the metal center, a feature that augurs well for applications in catalysis.

Ethylene Polymerization Studies of Pyridyl-Phosphinimine Metal Complexes

Preliminary ethylene polymerizations were performed to determine the catalytic potential of pyridyl-phosphinimine containing-transition metal catalysts compounds 36, 40, and 44. These compounds were found to be inactive towards polymerization of ethylene at room temperature and one atmospheric pressure of ethylene. when activated with MAO.

Also complexes 36, 40, and 44 were evaluated for ethylene oligomerization at 35°C and 300 psi ethylene. The in situ generation of the active species was performed by diethyl aluminum chloride (DEAC) in chlorobenzene. Under these reaction conditions, all the three the nickel species were found to be inactive towards oligomerization of ethylene.

The exocyclic late transition metal pyridyl-phosphinimine complexes which have been synthesized in this work appear to be inactive for both ethylene polymerization and oligomerization. The main reason for this, is the presence of a phosphinimine fragment that exerts a very different influence on the electronic properties of the metal center by decreases the positive charge on the active metal site leading to a weaker interaction with the ethylene. This conclusion was supported by computational studies on model systems of the active nickel (II) phosphinimine species performed by L. Spencer and J. Gauld. these
calculations also suggested that Modifications of the ligand with electron-withdrawing groups on the phosphorus atom could improve reactivity ethylene. To date, no phosphinimine ligands with electron withdrawing substituents have been reported in the literature.

The other reason related to this subject is that there is not sufficient steric protection around the metal center specially in case of 36 and 40 compared to the previously reported α-diimine system. Increasing the steric bulk around the metal by using more bulky substituents on the pyridine side may play important role in the complexes activity and this is also one of the future effort.
2.4 Summary and Conclusions

Synthesis of group 8 and 10 pyridyl-phosphinimine complexes \((36, 37, 38, 39, 40, 41, 42, 43\text{ and } 44)\) has been successfully developed. Activation of several of these complexes with DEAC or MAO results in no activity for the oligomerization or polymerization of ethylene. Computational calculations on model systems of the active nickel (II) phosphinimine species done at University of Windsor suggest that the phosphinimine ligand creates a greater negative charge on the metal centre than a diimine ligand, which translates into a weakened ethylene-metal interaction. Further, it was suggested that removal of the negative charge can be accomplished by the substitution of electron-withdrawing groups on the phosphorus atom.
Chapter Three

Synthesis of Chiral Nickel Diiminophosphorane Complexes

3.1 Introduction

Iminophosphoranes, or compounds with the general structure $R_3P=NR$, date back to 1919.\textsuperscript{41} Chiral diiminophosphorane compounds have been used as ylide building blocks for polymers that contain a P-N backbone (polyphosphazenes).\textsuperscript{63,64} However chiral diiminophosphoranes can also be used as ligands as they possess a highly polarized P=N bond which can coordinate to transition metals via the two sp$^2$-hybrized nitrogen atoms. There are two types of bidentate ligands incorporating two phosphinimine ($R_3P(NR')$) moieties as shown in Figure 3.1. Type A has a carbon backbone bridging the two nitrogen atoms and type B has a carbon backbone bridging the two phosphor atoms.$^{65-67}$

![Figure 3.1: Bidentate diiminophosphorane derivatives.](image)

The coordination chemistry of chiral diiminophosphorane ligands (type A) has been studied to some extent. A variety of transition metal complexes with these ligands (eg. Rh, Ni and Pd) have been isolated.$^{68-70}$ It should be noted that
these complexes are not active for ethylene oligomerization.\textsuperscript{71-74} Reetz \textit{et al} \textsuperscript{75} have developed some chelating chiral diiminophosphorane ligands such as 46.

![Figure 3.2: Chiral 1,2 diiminophosphorane chelating ligand.](image)

The ligand 46 was suitable for preparing a wide variety of chiral transition metal complexes such as the copper complex 47.

![Figure 3.3: Copper complex with chiral diiminophosphorane chelating ligands.](image)

Compound 47 was shown to be a good enantioselective catalyst for the cyclopropanation of styrene by ethyl diazoacetate as shown in Scheme 3.1.

![Scheme 3.1: Cyclopropanation of styrene](image)
In the above reaction the two products 48 and 49 were formed in equal amounts, each having an enantiomeric excess (ee) of 90% and 74% in favour of the absolute configurations (S, R) and (R, R), respectively.\textsuperscript{76}

In 2001 R. Réau\textsuperscript{77,78} also reported the synthesis of the nickel complexes 50, 51 and 52 with 1,2 diiminophosphorane ligands of type A and it was found that metal complexes of these ligands exhibit quite different steric and electronic prosperities than those of type A ligands. The key difference is that the bulky phosphine substituents in type B ligands are closer to the metal center which makes complexes like 51 have ethylene oligomerization activity of (344 g /mmol hr atm) while the same nickel complexes with type A showed no activity.\textsuperscript{79-81}

![Diagram of complexes 50, 51, and 52](image)

**Figure 3.4:** Nickel 1,2-diiminophosphorane complexes.

In this chapter the synthesis and characterization of neutral nickel 1,2 diiminophosphorane complexes that have the chiral ligand (R-1,1'-binaphthyl-2,2'-bis(iminotriphenylphosphine) 54 will be described. This was of interest because of their potential use in the polymerization of prochiral olefins. This could produce stereoregular polymers such as polypropylene. Potential applications of such polymers include thermoplastics, fibers, and thermoplastic elastomers.\textsuperscript{82}
3.2 Experimental

General Data. All preparations were performed under a dry, O₂-free nitrogen atmosphere employing Schlenk line techniques, or a vacuum atmosphere inert glovebox, unless otherwise stated. Unless otherwise mentioned, all organic chemicals were reagent grade and used as received from Aldrich Chemical Company. Diethyl ether, hexane, Benzene, methylene chloride, and toluene were either dried according to literature techniques⁵⁷ or obtained directly from an Innovative Technologies solvent purification system. Compounds 53 and 54 were prepared according to literature techniques with a slight modification.⁸³ ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on Bruker Avance 300 MHz NMR spectrometer operating at 300, 75, and 121 MHz, respectively. Some ¹H, ¹³C {¹H}, and ³¹P {¹H} NMR spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer operating at 500, 121, and 202 MHz, respectively. Trace amounts of protonated solvents were used as references and ¹H and ¹³C {H} chemical shifts are reported relative to tetramethylsilane (SiMe₄). ³¹P {¹H} spectra were externally referenced to 85% H₃PO₄. The ¹³C {¹H} resonances reported are all singlets unless otherwise noted. Elemental analyses were carried out by the Centre for Catalysis and Materials Research (CCMR), Windsor, Ontario, Canada. IR spectroscopy was performed on a Bruker Infrared Fourier Transform Spectrometer VECTOR 22.
Synthesis of [R-2,2'-diamino(triphenyl)Phosphine-1,1'-binaphthalene] (Phosphonium bromides) 53:

Compound 53 was prepared according to a modified literature method\(^3\), however, NMR data was not reported for this species. \(^{31}\)P {H} NMR (CD\(_2\)Cl\(_2\)): δ -6.6 (s), -4.7 (s), 27.3 (s). \(^1\)H NMR (CD\(_2\)Cl\(_2\)): δ 7.75 (d, 2H, J\(_{H-H}\) = 7.3 Hz ,H-5), 7.57 (d, 2H, J\(_{H-H}\) = 8.7 Hz, H-4), 7.38 (m, 12H, H-10), 7.34 (m, 6H, H-12), 7.20 (d, 2H, J\(_{H-H}\) = 8.3 Hz, H-8), 7.10 (t, 2H, J\(_{H-H}\) = 7.7 Hz, H-11), 7.08 (d, 2H, J\(_{H-H}\) = 1.4 Hz, H-6), 7.00 (d, 2H, J\(_{H-H}\) = 8.3 Hz, H-7), 6.91 (d, 2H, J\(_{H-H}\) = 8.6 Hz, H-3). \(^{13}\)C {H} NMR (CD\(_2\)Cl\(_2\)): δ 147.3, 135.70, 132.9, 132.6 (d, J\(_{C-P}\) = 10.1 Hz, C-9), 131.3 (d, J\(_{C-P}\) = 100 Hz, C-12), 129.9 (d, J\(_{C-P}\) = 2.7 Hz, C-1), 128.5 (s, C-4), 128.5 (d, J\(_{C-P}\) = 11.9 Hz, C-11), 127.7 (s, C-5), 126.4 (s, C-4), 126.0 (s, C-8), 125.8 (d, J\(_{C-P}\) = 8.1 Hz, C-3), 125.1 (s, C-7), 121.3 (s, C-6).

Synthesis of (R)-1,1'-binaphthyl-2,2'-bis(iminotriphenylphosphine) 54

Compound 54 was prepared according to modified literature method\(^3\), however, NMR data was not reported for this species. \(\nu_{P-H}\) 1105 cm\(^{-1}\) \(^{31}\)P {H} NMR (CD\(_2\)Cl\(_2\)): δ -4.6 (s). \(^1\)H NMR (CD\(_2\)Cl\(_2\)): δ 7.75 (d, 2H, J\(_{H-H}\) = 7.9 Hz, H-5), 7.57 (d, 2H, J\(_{H-H}\) = 8.8 Hz, H-4), 7.38 (m,12H, H-10), 7.34 (m, 6H, H-12), 7.20 (d, 2H, J\(_{H-H}\) = 8.3 Hz, H-8), 7.10 (t , 2H, J\(_{H-H}\) = 7.5 Hz, H-11), 7.08 (dd, 2H, J\(_{H-H}\) = 1.3 Hz, H-6), 7.00 (d, 2H, J\(_{H-H}\) = 8.3 Hz, H-7), 6.91 (d, 2H, J\(_{H-H}\) = 8.6 Hz, H-3). \(^{13}\)C {H} NMR (CD\(_2\)Cl\(_2\)): δ 147.3 (s, C-2), 135.7 (s, C-8), 132.9 (d, J\(_{C-P}\) = 10.1Hz, C-10), 132.6 (d, J\(_{C-P}\) = 100.2Hz, C-9), 131.3 (d, J\(_{C-P}\) = 2.7Hz, C-12), 130.0 (d, J\(_{C-P}\) = 21.6 Hz, C-1), 128.5 (s, C-4), 128.5 (d, J\(_{C-P}\) = 11.6 Hz, C-11), 127.7 (s, C-5), 126.4 (s, C-4), 126.0 (s, C-8), 125.8 (d, J\(_{C-P}\) = 8.1 Hz, C-3), 125.1 (s, C-7), 121.3
(s, C-6). Anal. Calcd. for C_{56}H_{42}N_{2}P_{2}: C, 83.56; H, 5.26; N, 7.69. Found C, 83.60; H, 5.89; N, 7.88.

Scheme 3.2: Synthesis of R-1,1'-binaphthyl-2,2'-bis(iminotriphenylphosphene) (54).

Synthesis of R-1, 1'-binaphthyl-2, 2'-bis(iminotriphenylphosphene)NiBr_{2}: 55:
To 40 mg (0.04 mmol) of NiBr_{2} (DME) adduct in 10 ml THF was added 100 mg (0.125 mmol) of the ligand 54. The green suspension was stirred overnight, and the mixture filtered to give 80 mg (80%) green powder. ν_{P=N} 807 cm\(^{-1}\) \(^{31}\)P \{H\} NMR (CD_{2}Cl_{2}): \(6\) 21.44 (s). \(^{1}\)H NMR (CD_{2}Cl_{2}) (br). Anal. Calcd. for C_{56}H_{42}N_{2}P_{2}NiBr_{2}: C, 66.73; H, 4.10; N, 2.73. Found C, 67.06, H, 4.95, N, 3.01.
Synthesis of R-1,1'-binaphthyl-2,2'-bis(iminotriphenylphosphine)NiCl₂ 56:
To 40 mg (0.04 mmol) of NiCl₂ (DME) adduct in 10 ml CH₂Cl₂ was added 100 mg (0.125 mmol) of the ligand 54. The mint green suspension was stirred overnight, and the mixture filtered and washed with 30 ml of ether and dried to give 80 mg (80%) Yield mint green powder. νₚ=ₙ 815 cm⁻¹. ³¹P {H} NMR (CD₂Cl₂): δ 21.50 (s). ¹H NMR (CD₂Cl₂) very broad signals. Anal. Calcd. for C₅₆H₄₂N₂P₂NiCl₂: C, 67.73; H, 4.72; N, 2.73. Found C, 68.10; H, 4.95; N, 3.00.

Scheme 3.3: Synthesis of neutral nickel chiral diiminophosphorane complexes 55 and 56
Procedure for ethylene oligomerization

A 500 mL Parr stainless steel autoclave was heated (~120°C) under vacuum for 2 hours. After cooling the autoclave to the desired temperature, a toluene solution of the activator diethylaluminumchloride (DEAC) and methylaluminoxane (MAO) was added under N₂. The solution was stirred for an additional hour, and a toluene/chlorobenzene solution of the metal complex was added. The vessel was quickly pressurized with 300 psi of ethylene, and the reaction stirred for 30 minutes. The autoclave was cooled to -78°C, and the volatiles were slowly vented. Ethanol (10 mL) and an internal standard were added (toluene for DEAC activation or diethyl ether for MAO activation) to quench the reaction, and the mixture was warmed to -40°C over 20 minutes. The composition of the alkenes formed was determined by GC and NMR spectroscopy.

General Information on X-Ray Data Collection and Reduction

The crystals was manipulated and mounted in a glass capillary in a glovebox, thus maintaining a dry, O₂-free environment. The diffraction study was performed with a Siemens SMART System CCD diffractometer. The data were collected for a hemisphere of data in 1329 frames with 10-second exposure times. The observed extinctions were consistent with the space group. A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collection. An empirical
absorption correction based on redundant data was applied to the data set. Subsequent solution and refinement was performed using the SHELXTL solution package.

**General Information of Structure Solution and Refinement**

Non-hydrogen atomic scattering factors were taken from the literature tabulations.\(^{74}\) The heavy atom positions were determined using direct methods. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on \(F\), minimizing the function \(\omega(\mid F_o \mid - \mid F_c \mid)^2\) where the weight \(\omega\) is defined as \(4F_o^2/2\sigma(F_o^2)\) and \(F_o\) and \(F_c\) are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. No disorder was indicated by the difference maps or the thermal parameters. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated, but not refined.
X-ray Structure Determination of 55 and 56

Data were collected at room temperature. No crystal decay was observed for any of the two compounds. ORTEP drawing of 55 and 56 are shown in Figures 3.2 and 3.4 respectively, with 30% thermal ellipsoids. Selected bond distances and angles are listed in the caption for Figures 3.1 and 3.2 respectively. Crystallographic parameters for both complexes are shown in Tables 3.1.
Table 3.1: Crystallographic Parameters for 55 and 56

<table>
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<tr>
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<th>56</th>
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<tr>
<td>Formula</td>
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<td>$\text{C}_5\text{H}_4\text{N}_2\text{PNiCl}_2$</td>
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<tr>
<td>MW</td>
<td>1022.46</td>
<td>933.56</td>
</tr>
<tr>
<td>$a$(Å)</td>
<td>13.652(8)</td>
<td>13.620(7)</td>
</tr>
<tr>
<td>$b$(Å)</td>
<td>18.887(10)</td>
<td>18.650(9)</td>
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<tr>
<td>$c$(Å)</td>
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<td>19.403(10)</td>
</tr>
<tr>
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<td>90</td>
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<tr>
<td>$\beta$(deg)</td>
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<td>Orthorhombic</td>
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<tr>
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<td>$\text{P2}_1\text{2}_1\text{2}_1$</td>
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<tr>
<td>$\text{Vol}(\text{Å}^3)$</td>
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<td>4929(4)</td>
</tr>
<tr>
<td>$D_{\text{calcd}}$ (gcm$^{-1}$)</td>
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<td>1.374</td>
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<td>$Z$</td>
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<td>4</td>
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<tr>
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<td>Variables</td>
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<tr>
<td>Goodness of Fit</td>
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<td>1.056</td>
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</table>

$^a$All data collected at 20°C with Mo Kα radiation ($\lambda = 0.71073$ Å), $R = \Sigma |F_o|-|F_c|}/\Sigma |F_o|$, $R_w = [\Sigma [\omega(F_o^2-F_c^2)^2]/\Sigma [\omega F_o^2]]^{0.5}$
Results and Discussions.

The phosphonium bromide intermediate 53 was obtained by the addition of the a primary amine R-2,2'-diamino-1.1'-binaphthalene and 2 equiv triethylamine to triphenylphosphine dibromide in benzene. \(^1\)H NMR spectroscopy showed the expected resonances while \(^{31}\)P NMR showed three singlets at -6.6, -4.7 and 27.3 ppm. The deprotonation of the dibromide salts with excess potassium hydroxide in presence of activated molecular sieves yielded the desired ligand 54. \(^1\)H NMR data revealed minor changes from the dibromide intermediate product, while the \(^{31}\)P NMR spectrum revealed a singlet at -4.6 ppm. The IR spectrum of the ligand shows a strong N=P stretching band around 1105 cm\(^{-1}\). The ligand was reacted with both nickel dibromide and nickel dichloride dimethoxy ethane adducts in appropriate solvents to give both the desired metal complexes \((L)\text{NiBr}_2\) 55, and \((L)\text{NiCl}_2\) 56 as shown in Scheme 3.5. Both complexes were characterized by NMR and IR spectroscopy, and X-ray diffraction.

![Diagram of reaction and complexes](image)

\(M=\text{Ni (55), (56)}\)
\(X=\text{Br, Cl}\)

**Scheme 3.4:** General synthesis of chiral nickel diiminophosphoranes complexes 55 and 56
Figure 3.5: ORTEP drawing of 55, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Ni(1)-N(1) 2.014(7) Å, Ni(1)-N(2) 2.028 Å, Ni(1)-Br(1) 2.3916(17) Å, Ni(1)-Br(2) 2.4296(19) Å, P(1)-N(1) 1.615(7) Å, P(2)-N(2) 1.607(7) Å, N(1)-C(1) 1.443(10) Å, N(2)-C(11) 1.436(10) Å, N(2)-Ni(1)-N(1) 102.2(3)°, N(2)-Ni(1)-Br(1) 101.5(2)°, N(1)-Ni(1)-Br(1) 104.77(19)°, N(2)-Ni(1)-Br(2) 109.3(2)°, N(1)-Ni(1)-Br(2) 103.40(19)°, Br(1)-Ni(1)-Br(2) 132.09(6)°.
Figure 3.6: ORTEP drawing of 56, 30% thermal ellipsoids are shown hydrogen atoms have been omitted for clarity. Ni(1)-N(1) 2.021(3) Å, Ni(1)-N(2) 2.036(3) Å, Ni(1)-Cl(2) 2.2490(14) Å, Ni(1)-Cl(1) 2.2815(17) Å, P(1)-N(1) 1.608(3) Å, P(2)-N(2) 1.607(3) Å, P(1)-C(27) 1.798(4) Å, N91-C(1) 1.446(4) Å, N(2)-C(11) 1.445(4) Å, N(2)-Ni(1)-N(1) 101.33(11)°, N(2)-Ni(1)-Cl(2) 101.28(9)°, N(1)-Ni(1)-Cl(1) 109.24(9)°, N(2)-Ni(1)-Cl(1) 103.67(9)°, N(1)-Ni(1)-Cl(2) 103.78(9)°, Cl(1)-Ni(1)-Cl(2) 133.34(5)°.
Both nickel complexes 55 and 56 were subjected to an X-ray diffraction study in order to evaluate the influence of the carbon backbone rigidity on the coordination behavior of the chiral diiminophosphorane ligand. For both complexes the nickel atom is located in a distorted tetrahedral coordination environment consisting of two halides and two N donor atoms of the bidentate chiral diiminophosphorane moiety. The Ni-Cl bond lengths are (2.2490(14) and 2.2815(17) Å), while the Ni-Br bond lengths are (2.3916(17) and 2.4296(19) Å) Å these agree with bond lengths in similar compounds that have been reported in the literature. The Ni(1)-N(1) and Ni(1)-N(2) bond lengths are also similar for both complexes and these ranged from 2.021(3) Å to 2.028(3) Å. The P-N bond lengths in 55, and 56 ranged from 1.607(7) Å to 1.615(7) Å which typical for N-P bond. These structural data conform that the chiral diiminophosphorane ligands act as chelates. These features prompted us to investigate the use of these complexes as catalysts for ethylene polymerization and polymerization of prochiral olefins such as propylene.
3.3 Ethylene polymerization Studies by Nickel bis-phosphinimine Complexes

Preliminary ethylene oligomerization was performed to determine the effect of the carbon backbone of the bis-phosphinimine ligand of type A (Figure 3.1) on the metal center. Initial testing of complexes 55 and 56 at room temperature and atmospheric ethylene pressure in a Buchi reactor showed no polymerization or oligomerization activity. Complexes 55 and 56 were then activated with MAO in toluene or diethyl aluminum chloride (DEAC) in chlorobenzene at 35°C and 300 psi ethylene in a Parr high pressure reactor. No polymer was recovered after each trial.

The two complexes appear to be inactive for ethylene polymerization. The lack of activity might be due to steric or electronic properties of these chiral derivatives. The two phosphinimine donors make the nickel less acidic which may weaken interactions between nickel and ethylene. It is assumed that these complexes will be also inactive for propylene polymerization. Reducing the steric congestion the phosphinimine fragment and adding electron withdrawing substituents on the phosphorus atom may increase the catalytic activity of these complexes.
3.4 Summary and Conclusions

A synthetic method for the preparation of nickel chiral diiminophosphane complexes 55 and 56 has been developed. Activation of these complexes with DEAC or MAO result in no activity for both ethylene polymerization and propylene polymerization due to the steric effect. These chiral complexes may find utility in other asymmetric reactions such as cyclopropanation of styrene by ethyl diazoacetate. This will be target of future efforts.
Chapter Four

Summary and Outlook

Syntheses and use of exocyclic pyridyl phosphinimine and chiral diiminophosphorane ligands in late transition metal catalyzed ethylene polymerization reactions has been accomplished in this research. The main objective of this work was to develop phosphinimine ligand alternatives to the previously reported α-diiimine ligands. Some of these complexes with these types of ligands were evaluated as possible catalysts for olefin polymerization.

In Chapter two, the syntheses of several pyridyl-phosphinimine complexes of nickel, iron, cobalt and palladium were described. These prospective catalysts were activated with both MAO and DEAC in the presence of ethylene to determine their catalytic potential. Unfortunately, all of complexes were ineffective in polymerizing and oligomerizing ethylene. These results stand in contrast to the related nickel α-diiimine complexes.

The synthesis of chiral diiminophosphorane metal complexes was described in chapter three. The chiral diiminophosphorane ligand fragment was reacted with nickel(II) halides to give complexes 55 and 56. These complexes were evaluated as possible catalysts for olefin polymerization. It was found to be inactive towards of ethylene polymerization and therefore was not tested for polymerization of α-olefins.

The research and polymerization activities described in this thesis have provided valuable insight into the applications of exocyclic pyridyl-phosphinimine late transition metal complexes and chiral diiminophosphorane nickel complexes
in polymerization and oligomerization of both ethylene and α-olefins. Continued research will be aimed at modifying the phosphinimine ligands through the incorporation of electron-withdrawing groups and decreasing the steric bulk group on the chiral diiminophosphorane ligand in order to maximize the activity of catalysts and also exert greater alkene selectivity. Using these complexes such as 55 and 56 as enantioselective catalysis for cyclopropanation of styrene by ethyl diazoacetate is also a target for future efforts.

In conclusion, the research presented herein has provided good background for future applications of both exocyclic pyridyl-phosphinimine and chiral diiminophosphorane ligands in late transition metal catalysis.
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